

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 426 638 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
24.04.1996 Bulletin 1996/17

(51) Int Cl.⁶: **C08F 4/602, C08F 10/00**

(21) Application number: **90870175.8**

(22) Date of filing: **09.10.1990**

(54) Addition of aluminium alkyl for improved metallocene catalyst

Addition von Alkylaluminium zum Verbessern eines Metallocenkatalysators

Addition d'alkylaluminium pour un catalyseur métallocène amélioré

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: **30.10.1989 US 419222**

(43) Date of publication of application:
08.05.1991 Bulletin 1991/19

(73) Proprietor: **FINA TECHNOLOGY, INC.**
Dallas, Texas 75206 (US)

(72) Inventors:
• **Ewen, John A.**
Houston, Texas 77058 (US)
• **Elder, Michael J.**
Friendswood, Texas 77546 (US)

(74) Representative: **Leyder, Francis et al**
c/o Fina Research S.A.
Zone Industrielle C
B-7181 Feluy (BE)

(56) References cited:
EP-A- 0 206 794 **EP-A- 0 277 004**
US-A- 3 709 853

- **JOURNAL OF POLYMER SCIENCE/PART A:
POLYMER CHEMISTRY, vol. 26, no. 11, October
1988, pages 3089-3102, New York, NY, US;
J.C.W. CHIEN et al.:
"Metallocene-methylaluminoxane catalysts for
olefin polymerization. I. Trimethylaluminum as
coactivator"**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 426 638 B1

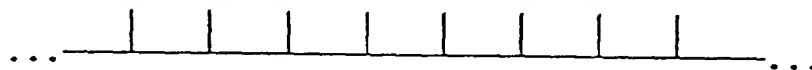
Description

FIELD OF THE INVENTION:

This invention relates, in general, to an improved catalyst system and, specifically, to an improved metallocene catalyst system for polymerisation of olefins by addition of an aluminum alkyl and a process for using such a catalyst.

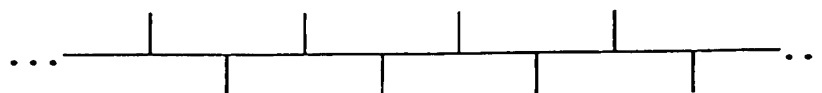
DESCRIPTION OF RELATED ART:

Olefins, especially propylene, may be polymerised to form polyolefins in various forms: isotactic, syndiotactic and atactic. Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as



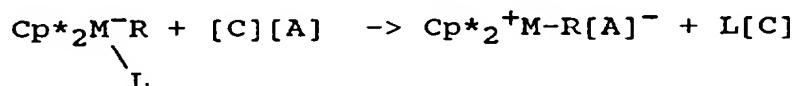
Isotactic polypropylene is capable of being a highly crystalline polymer with a crystalline melting point and other desirable physical properties that are considerably different from the polymer in an amorphous (noncrystalline) state.

A syndiotactic polymer contains principally units of exactly alternating stereo isomers and is represented by the structure:



A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

Polymerization of olefins is primarily with Ziegler-Natta catalysts. One family of Ziegler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane as a cocatalyst. It has been demonstrated that a Ziegler-Natta catalyst for olefin polymerization can be formed by combining a Group IV metallocene with an ionic compound.



Cp - pentamethylcyclopentadienyl

M - Group IV metal

R - alkyl

L - ligand

[C] - cation

[A] - anion

The resulting compound is a metallocene cation which acts as catalyst. The cation [C] of the ionic compound reacts with the metallocene to generate an ion pair. The anion, [A], is not coordinated or is only loosely coordinated with the cationic metallocene.

The following methods have been used to produce the above reaction:

One-Electron Oxidation - This method is illustrated in "Ethylene Polymerisation by a Cationic Dicyclopentadienylzirconium(IV) Alkyl Complex", R.F. Jordan, c.S.Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc., p. 7410-7411, Vol. 108 (1986). These early examples used a Lewis base to make the metal cation less electrophilic and [BPh₄]⁻ was the anion where Ph is C₆H₅. The reaction occurred in a solvent which was coordinated with the cation. These materials were usually of low activity.

Protonation - This method is illustrated by "Synthesis and Insertion Reactions of Cationic Alkylbis(cyclopentadienyl) titanium Complexes", M. Bochmann, L.M.Wilson, J. Chem. Soc. Commun., p. 1610-1611, (1986); "Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L. Wilson, Organometallics, p. 2556-2563, Vol. 6, (1987); "Insertion Reactions of Nitriles in Cationic Alkylbis(cyclopentadienyl)titanium Complexes", M. Bochmann, L. Wilson, Organometallics, p. 1147-1154, Vol. 7 (1987).

European Patent Application 0-277-003 relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with a compound having a cation capable of donating a proton and an anion having a plurality of boron atoms. For example, the following reaction illustrates the invention:

bis(cyclopentadienyl)hafnium dimethyl + N,N-dimethylanilinium bis(7,8-dicarbaundecaborato) cobaltate(III) \rightarrow $[\text{Cp}_2\text{HfMe}][\text{B}] + \text{CH}_4 + \text{N,N-dimethylaniline}$
 where [B] is 7,8-dicarbaundecaborane.

European Patent Application 0-277-004 also relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with an ionic compound having a cation which will irreversibly react with a ligand on the metal compound and an anion having a plurality of lipophilic radicals around a metal or metalloid ion. For example, the following reaction illustrates the invention:

tri(n-butyl)ammonium tetra(pentafluorophenyl) boron + bis(cyclopentadienyl) zirconium dimethyl $\rightarrow [\text{Cp}_2\text{ZrMe}][\text{BPh}_4] + \text{CH}_4 + \text{tri(n-butyl)N}$

A by-product of the protonation reaction is a Lewis base (amine) some of which can coordinate to the cations and thus inhibit catalyst activity. Starting materials must be chosen carefully to avoid generating particular amines which are catalyst poisons.

Carbonium Ion Chemistry - This method is illustrated by "Multiple Metal-Carbon Bonds", R. R. Schrock, P. R. Sharp, J. Am. Chem. Soc., p.2389-2399, Vol. 100, No. 8 (April, 2, 1978). A problem with both the carbonium ion chemistry method and the protonation method is that they are poisoned by basic impurities found in olefins and solvents, often resulting in runaway reactions. The high reaction temperature (over 100° C) and the short duration of the polymerisation results in short chain lengths and low molecular weight.

Metallocene catalysts are sensitive to poisons in the absence of a scavenging agent, such as methylaluminoxane. Polymerisation requires high concentrations of the cations and frequently end up as either runaway reactions or yield no polymer at all.

SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a process for improving metal locene catalyst activity in polymerisation of olefins.

And, it is an object of this invention to use aluminum alkyl as a scavenging agent for poisons which reduce metallocene catalyst activity.

Also, it is an object of this invention to use aluminum alkyl to improve metal locene catalyst activity of a catalyst made by the protonation, carbonium ion chemistry or one electron oxidation method.

Further, it is an object of this invention to reduce cost of a metallocene catalyst system.

Additionally, it is an object of this invention to eliminate methylaluminoxane (MAO) as a cocatalyst in polymerization of propylene.

As well, it is an object of this invention to produce a metallocene catalyst which effects a controlled polymerization of olefins without a methylaluminoxane cocatalyst.

These and other objects are accomplished by mixing an aluminum alkyl with an olefin, preparing a metallocene catalyst, then mixing the catalyst with the aluminum alkyl-olefin mixture without a methylaluminoxane cocatalyst. The metallocene catalyst is an ion pair formed from a neutral metallocene compound and an ionizing compound.

DESCRIPTION OF THE INVENTION

The invention is for a process of polymerizing olefins without use of a methylaluminoxane cocatalyst and for a catalyst system for use in such a process. An aluminum alkyl is mixed with an olefin and then introduced into the presence of an ionic metallocene catalyst produced by mixing a neutral metallocene compound with an ionizing agent. Molar ratios for metallocene:ionizing compound:aluminum alkyl range from 0.5:1:0.5 to 5:1:350 and are preferably from 0.625:1:1.5 to 1.5:1:77 and are most preferably 1:1:1.

In one example of a new synthesis procedure for a metallocene catalyst, an ionizing ionic compound, such as triphenylcarbonium tetrakis(pentafluorophenyl)borate, is mixed with a neutral methyl derivatives of metallocene of the general formula Cp_2MR_p to produce the following reaction:



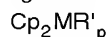
where Cp is cyclopentadienyl or substituted cyclopentadienyl, M is a Group III, IV, V or VI metal, R is a hydride, a halogen, an amide or a hydrocarbyl radical, except when R is a hydride only one R is a hydride, p is 1 to 4, C* is a carbonium, oxonium or sulfonium cation, A* is an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene and $[\text{C}^*][\text{A}^*]$ is an ionizing agent which does not contain an active proton. Each Cp can be the same or different. Each R can be the same or different. M is preferably titanium, zirconium or hafnium. R is preferably an alkyl, aryl, alkenyl, alkylaryl, or arylalkyl radical of up to 20 carbon atoms and is most preferably methyl. Cp_2MR_p is preferably ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)hafnium dimethyl, ethylene bis(indenyl)zirconium dimethyl or isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl and most preferably eth-

ylenebis(indenyl)zirconium dimethyl. Each reactant is placed in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation, such as methylene chloride or toluene. The preferred solvent is toluene.

The two reactants dissolved separately in the same solvents are mixed together at room temperature. The ionizing compound ionizes the metallocene and an ion pair is formed in which the metallocene cation acts as a catalyst. After mixing, the mixture is added to an olefin under conditions to effect polymerization. The olefin is preferably propylene. This procedure is covered by European Patent Application No. 90870174.1 which is hereby incorporated by reference into this application.

In another example of a synthesis procedure for a catalyst, two components, the first being a neutral methyl derivative of a metallocene, such as a bis(cyclopentadienyl) metal compound, containing at least one substituent capable of reacting with a proton and the second being an ionic compound with a cation capable of donating a proton and an anion which is a coordination complex of a plurality of lipophilic radicals and a metal. The anion is bulky, labile and capable of stabilizing the metal cation formed as a result of the reaction between the two compounds. A proton provided by the cation reacts with a ligand of the metallocene. An active catalyst is recovered as a direct product or decomposition product of the reaction. This is the protonation method described above. The above procedure is covered by European Patent Application Publication No. 0-277-004 which is hereby incorporated by reference into this application.

The neutral derivative of the metallocene is of the general formula:

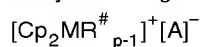


Wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R' is a hydride, a halogen, an amide or a hydrocarbyl radical, except when R' is a hydride only one R' is a hydride and p is from 1 to 4. M is preferably titanium, zirconium or hafnium and is most preferably zirconium. R' is preferably an alkyl, an aryl, an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms. The neutral derivative of the metallocene is preferably ethylene bis(tetrahydroindenyl)zirconium dimethyl or ethylene bis(indenyl)zirconium dimethyl and is most preferably ethylene bis(indenyl)zirconium dimethyl. The ionic compound is preferably N,N-dimethylanilinium tetrakis(pentafluorophenyl) boronate.

In another example of a synthesis procedure for a catalyst, a neutral derivative of a metallocene, such as a cyclopentadienyl metal compound, is combined with a tetraphenylborate metal compound. The neutral metallocene compound is of the general formula $\text{Cp}_2\text{MR}''_2$ or $\text{Cp}_2\text{MR}''\text{X}$ where Cp is cyclopentadienyl or substituted cyclopentadienyl, M is a Group III, IV, V or VI metal, X is a halogen and R'' is an alkyl. An X^- or R^- is abstracted from the metallocene by the metal of the tetraphenylborate metal compound, resulting in an ion pair of the general formula $[\text{Cp}_2\text{MR}'']^+ [\text{BPh}_4]^-$ where BPh_4 is a tetraphenyl borate anion.

An aluminum alkyl is mixed with an olefin and brought to reaction temperature. The aluminum alkyl is of the general formula AlR_3 where R is a halogen, oxygen, hydride, alkylalkoxy or aryl, each R being the same or different and at least one R is a alkyl. The aluminum alkyl is preferably trimethylaluminum (TMA) or triethylaluminum (TEA1) and is most preferably triethylaluminum. The olefin is any of the olefins but is preferably propylene or ethylene and is most preferably propylene. The mixture of aluminum alkyl and olefin is brought in contact with a metallocene catalyst. The catalyst may be made by any known method, including but not limited to those described above.

The catalyst system is an ionic metallocene catalyst of the general formula:



wherein $[\text{Cp}_2\text{MR}^{\#}_{p-1}]^+$ is a metallocene cation wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal, R# is a hydride, a halogen, an amide or a hydrocarbyl radical, each R# being the same or different, except if R# is a hydride only one R# is a hydride, p is from 1 to 4 and $[\text{A}]^-$ is an anion. R# is preferably a hydrocarbyl radical, such as an alkyl, an aryl, an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms and is most preferably an alkyl or alkoxy of up to six carbon atoms or an aryl of up to 10 carbon atoms. M is preferably a Group IV metal, such as titanium, zirconium and hafnium and is most preferably zirconium or hafnium. The metallocene cation is preferably a cation of ethylenebis(tetrahydroindenyl)zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl, ethylenebis(indenyl)hafnium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl and is most preferably ethylenebis(tetrahydroindenyl)zirconium dimethyl. The anion is preferably tetrakis(pentafluorophenyl)borate. The aluminum is as described above and is most preferably TMA or TEA1 and is most preferably TEA1.

The following metallocene-ionizing agent systems were evaluated with and without addition of an aluminum alkyl:

1. $\text{Et}(\text{Ind})_2\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
2. $\text{Et}(\text{Ind})_2\text{HfMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
3. $\text{Et}(\text{Ind})_2\text{ZrMe}_2/[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$
4. $i\text{Pr}(\text{Cp}-1\text{-Flu})\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
5. $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2/[\text{Ph}_3\text{C}][\text{BPh}^*_4]$
6. $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2/[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$

Et(Ind)₂ZrMe₂ is ethylene bis(indenyl)zirconium dimethyl, iPr(Cp-1-Flu)ZrMe₂ is isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl, Et(H₄Ind)₂ZrMe₂ is ethylene bis(tetrahydroindenyl)zirconium dimethyl [Ph₃C] [BPh⁺₄] is triphenylcarbenium tetrakis(pentafluorophenyl)boronate, (Me₂PhN)[BPh⁺₄] is N,N-dimethylanilinium tetrakis(pentafluorophenyl)boronate.

The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

GROUP 1:

EXAMPLE I

100 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 10 ml of toluene. 60 mg of Et(Ind)₂ZrMe₂ was dissolved in 10 ml of toluene. The two solutions were mixed together for 5 minutes at room temperature.

Reactor temperature was set to 50°C and one liter of propylene was pumped into the reactor. The catalyst mixture was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 50°C and the contents of the reactor were agitated for sixty minutes. At the end of the polymerization, the reactor is cooled and the unreacted propylene was vented from the reactor.

The reaction product was dried under vacuum at approximately 40°C for 12 hours. The polymer was then weighed and analysed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

EXAMPLE II

The procedure of Example 1 was repeated with the contents of the reactor being agitated for 30 minutes. The results are shown in Table I.

EXAMPLE III

The procedure of Example 1 was repeated with the contents of the reactor set point temperature being set at 70°C. The results are shown in Table I.

EXAMPLE IV

0.32 mmol of trimethylaluminum (TMA) was dissolved in 5 ml of toluene and was added to a 2 liter Zipperclave reactor under 5 psig of nitrogen. Reactor temperature was set to 70°C and one liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

100 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 10 ml of toluene. 60 mg of Et(Ind)₂ZrMe₂ was dissolved in 10 ml of toluene. The two solutions were mixed together for 5 minutes at room temperature.

The catalyst mixture was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 70°C and the contents of the reactor were agitated for sixty minutes. At the end of the polymerization, the reactor is cooled and the unreacted propylene was vented from the reactor.

The reaction product was dried under vacuum at approximately 40°C for 12 hours. The polymer was then weighed and analyzed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

EXAMPLE V

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1) and agitating the contents of the reactor for 10 minutes. The results are shown in Table I.

EXAMPLE VI

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 50 mg of triphenylcarbe-

nium tetrakis(pentafluorophenyl) boronate and 30 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for 5 minutes. The results are shown in Table I.

EXAMPLE VII

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 16 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 10 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for ten minutes. The results are shown in Table I.

EXAMPLE VIII

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for sixty minutes. The results are shown in Table I.

EXAMPLE IX

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 1.25 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for sixty minutes. The results are shown in Table I.

EXAMPLE X

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE XI

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for forty minutes. The results are shown in Table I.

EXAMPLE XII

The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 8 mg of triphenylcarbenium tetrakis(pentafluorophenyl)boronate and 5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE XIII

The procedure of Example II was repeated with 5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 8 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.66 mmol of triethyl aluminum and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XIV

The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 8 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.66 mmol of triethyl aluminum and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XV

The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 4 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.66 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XVI

The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 4 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.99 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XVII

The procedure of Example II was repeated with 2.5 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$, 24 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.66 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XVIII

The procedure of Example II was repeated with 2.5 mg $\text{Et(Ind)}_2\text{ZrMe}_2$, 24 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 2.00 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

GROUP 2:

EXAMPLE XIX

The procedure of Example II was repeated with 20 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$, 80 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.42 mmol of trimethyl aluminum and a run time of 30 minutes. The results are shown in Table I.

GROUP 3:

EXAMPLE XX

The procedure of Example 1 was repeated with 2.5 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$, 7 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXI

The procedure of Example II was repeated with 2.5 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$, 7.0 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, 0.66 mmol triethyl aluminum and a run time of 5 minutes. The results are shown in Table I.

EXAMPLE XXII

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 7.0 mg of N, N-dimethylanilinium tetrakis(pentafluorophenyl)boronate and 2.5 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$. The contents of the reactor were agitated for twenty-five minutes. The results are shown in Table I.

EXAMPLE XXIII

The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 3.5 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boronate and 1.25 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE XXIV

The procedure of Example II was repeated with 1.25 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$, 3.5 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, 0.66 mmol of triethylaluminum and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXV

The procedure of Example II was repeated with 0.625 mg of $\text{Et(Ind)}_2\text{ZrMe}_2$, 1.75 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, 0.66 mmol of triethylaluminum and a run time of 60 minutes. The results are shown in Table I.

GROUP 4:

EXAMPLE XXVI

The procedure of Example I was repeated with 40 mg of $\text{iPr(Cp-1-Flu)ZrMe}_2$, 60 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXVII

The procedure of Example I was repeated with 60 mg of $i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$, 100 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXVIII

The procedure of Example II was repeated with 60 mg of $i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$, 100 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.16 mmol of trimethylaluminum and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXIX

The procedure of Example II was repeated using 0.48 mmol of trimethylaluminum (TMA), 100 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ and 60 mg of $i\text{Pr}(\text{Cp-1-flu})\text{ZrMe}_2$, and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXX

The procedure of Example II was repeated with 20 mg of $i\text{Pr}(\text{Cp-1-Flu})\text{ZrMe}_2$, 60 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.16 mmol of trimethylaluminum and a run time of 60 minutes. The results are shown in Table I.

GROUP 5:

EXAMPLE XXXI

The procedure of Example 1 was repeated with 15 mg of $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$, 30 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXXII

The procedure of Example 1 was repeated with 20 mg of $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$, 40 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXXIII

The procedure of Example 1 was repeated with 20 mg of $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$, 40 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, and a run time of 5 minutes. The results are shown in Table I.

EXAMPLE XXXIV

The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$, 8 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.66 mmol of TEA1 and a run time of 60 minutes. The results are shown in Table I.

GROUP 6:

EXAMPLE XXXV

The procedure of Example 1 was repeated with 50 mg of $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$, 40 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, and a run time of 120 minutes. The results are shown in Table I.

EXAMPLE XXXVI

The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$, 9.2 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, 0.66 mmol of TEA1 and a run time of 60 minutes. The results are shown in Table I.

The following results are from the experimental runs described above using the method of the present invention.

TABLE I

Run #	Catalyst umol (mg)	Ionizing Agent umol (mg)	Al-alkyl mmol	Run Time min.
1	Et(Ind) ₂ ZrMe ₂ 159(60)	[Ph ₃ C][BPh* ₄] 109(100)	0	60
2	159(60)	109(100)	0	30
3	159(60)	109(100)	0	60
4	159(60)	109(100)	TMA 0.32	60
5	159(60)	109(100)	TEA1 0.33	10
6	80(30)	54(50)	0.33	5
7	26.5(10)	17.3(16)	0.33	10
8	6.63(2.5)	8.64(8)	0.66	60
9	3.36(1.25)	8.64(8)	0.66	60
10	6.63(2.5)	8.64(8)	0.66	30
11	6.63(2.5)	8.64(8)	0.66	40
12	13.3(5)	8.6(8)	0.33	30
13	13.3(5)	8.64(8)	0.66	30
14	6.63(2.5)	8.64(8)	0.66	60
15	6.63(2.5)	4.3(4)	0.66	30
16	6.63(2.5)	4.3(4)	0.99	30
17	6.63(2.5)	26(24)	0.66	30
18	6.63(2.5)	26(24)	2.00	30
19	Et(Ind) ₂ HfMe ₂ 53(20)	[Ph ₃ C][BPh* ₄] 85(80)	TMA 0.42	30
20	Et(Ind) ₂ ZrMe ₂ 6.6(2.5)	[Me ₂ PhN][BPh* ₄] 8.7(7.0)	0	60
21	6.6(2.5)	8.7(7.0)	TEA1 0.66	5
22	6.6(2.5)	8.7(7.0)	0.66	25
23	3.3(1.25)	4.35(3.5)	0.66	30
24	3.3(1.25)	4.35(3.5)	0.66	60
25	1.65(.0625)	2.175(1.75)	0.66	60
26	iPr(Cp-1-Flu)ZrMe ₂ 102(40)	[Ph ₃ C][BPh* ₄] 65(60)	0	60
27	154(60)	109(100)	0	60
28	154(60)	109(100)	TMA 0.16	60
29	154(60)	109(100)	0.48	60
30	51(20)	65(60)	0.16	60
31	Et(H ₄ Ind) ₂ ZrMe ₂ 40(15)	[Ph ₃ C][BPh* ₄] 33(30)	0	60
32	53(20)	44(40)	0	60
33	80(30)	67(60)	0	5
34	7(2.5)	8.8(8.0)	TEA1 0.66	60
35	Et(H ₄ Ind) ₂ ZrMe ₂ 133(50)	[Me ₂ PhN][BPh* ₄] 44(40)	0	120
36	7(2.5)	10(9.2)	TEA1 0.66	60

Run #	Polymeri- zation Temp (°C)	Yield (gms)	Melting Temp (°C)
1	50	19	137
2	50	11	125
3	70	8	126
4	70	270	124
5	70*	340	126
6	70*	432	No Melt
7	70*	260	118
8	70	319	129
9	70	89	132
10	70	117	
11	70*	377	131
12	70	22	132
13	70	51	131
14	70*	357	127
15	70	9	132
16	70	11	134
17	70	149	131
18	70	62	130
19	70	51	131
20	70	-	-
21	70*	106	125
22	70*	405	127
23	70*	434	127
24	70	385	131
25	70	253	131
26	80	2	-
27	70	51	-
28	70*	284	116
29	70*	268	117
30	70*	156	116
31	50	2	142
32	50	35	138
33	120	70	127
34	70	154	115
35	50	50	133
36	70	116	116

*Exotherm; reaction temperature increased by more than 10°C.

The process described by this invention synthesizes cations which are used as catalysts in olefin polymerization. The process of making catalysts with this invention produces catalysts having high activity and reduces the by-products which can inhibit catalyst activity. This new synthesis also reduces the catalyst poisons found in the solvents which can inhibit catalyst activity.

The addition of an aluminum alkyl to ionic metallocene catalyst systems was found to result in reproducible, controllable, high efficiency polymerizations. The addition of an alkyl aluminum provides a scavenging agent for catalyst poisons. The quantity of aluminum alkyl added is relatively small and aluminum alkyls are relatively inexpensive. The metallocene cation/aluminum alkyl combination results in a better catalyst system than the cations alone and give consistently high activities.

Claims

1. A process for polymerization of olefins comprising:

- mixing an aluminum alkyl with an olefin;
- preparing a metallocene catalyst;
- mixing the catalyst with the aluminum alkyl-olefin mixture.

wherein the aluminum alkyl is of the general formula AlR_3 where R is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl;

wherein the metallocene is an ion pair formed from a neutral metallocene compound and an ionizing ionic compound, said ion pair comprising a metallocene cation and an anion from the ionizing ionic compound;
 wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation.

2. A process as recited in Claim 1 wherein R is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.

3. A process as recited in Claim 2 wherein the molar ratio for metallocene:ionizing compound:aluminum alkyl ranges from 0.5:1:0.5 to 5:1:350.

4. A process as recited in Claim 3 wherein the molar ratio for metallocene:ionizing compound:aluminum alkyl ranges from 0.625:1:1.5 to 1.5:1:77.

5. A process as recited in Claim 4 wherein the molar ratio for metallocene:ionizing compound:aluminum alkyl is 1:1:1.

6. A process as recited in Claim 5 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.

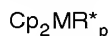
7. A process as recited in Claim 6 wherein the aluminum alkyl is triethylaluminum.

8. A process as recited in Claim 1 wherein the catalyst is prepared by the following steps comprising:

a) mixing an ionizing ionic compound with a neutral metallocene; and

b) allowing contact between the ionizing ionic compound and the neutral metallocene to generate an ion pair in which the metallocene cation acts as a catalyst;

wherein the neutral metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R^* is a hydride, a halogen, an amide or a hydrocarbyl radical, each R^* being the same or different, except when R^* is a hydride only one R^* is a hydride and p is from 1 to 4;

wherein the ionizing ionic compound does not contain an active proton and contains a carbonium, oxonium or sulfonium cation; and

wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.

9. A process as recited in Claim 8 wherein the olefin is propylene.

10. A process as recited in Claim 7 wherein R is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.

11. A process as recited in Claim 10 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.

12. A process as recited in Claim 11 wherein the M is hafnium or zirconium.

13. A process as recited in Claim 12 wherein the neutral methyl derivative of a metallocene is chosen from the group consisting of ethylenebis(tetrahydroindenyl) zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl, ethylene bis(indenyl)hafnium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl.

14. A process as recited in Claim 13 wherein the ionizing ionic compound is triphenylcarbenium tetrakis(pentafluorophenyl)boronate.

15. A process as recited in claim 1 wherein the catalyst is prepared by the following steps comprising:

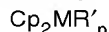
a) combining, in a suitable solvent or diluent, at least one first compound consisting of a neutral methyl derivative of a metallocene containing at least one substituent capable of reacting with a proton, the metallocene containing a metal selected from the group consisting of titanium, zirconium and hafnium and at least one second compound comprising a cation, capable of donating a proton, and an anion formed as a result of the reaction between the two compounds;

b) maintaining the contact in step a) for sufficient period of time to permit the proton provided by the cation of the second compound to react with a ligand of the first compound; and

c) recovering an active catalyst as a direct product or as a decomposition product of one or more of the direct products from step b).

16. A process as recited in Claim 15 wherein the olefin is propylene.

17. A process as recited in Claim 16 wherein the neutral methyl derivative of a metallocene is of the general formula:



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, M is a Group III, IV, V or VI metal, R' is hydrocarbyl radical, each R' being the same or different, and p is from 1 to 4.

18. A process as recited in Claim 17 wherein the M is selected from the group consisting of titanium, zirconium and hafnium.

19. A process as recited in Claim 18 wherein the M is zirconium.

20. A process as recited in Claim 19 wherein R' is selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.

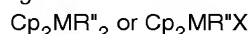
21. A process as recited in Claim 10 wherein the neutral methyl derivative of a metallocene is chosen from the group consisting of ethylene bis(tetrahydroindenyl) zirconium dimethyl and ethylene bis(indenyl)zirconium dimethyl.

22. A process as recited in Claim 21 wherein the first compound is ethylene bis(indenyl)zirconium dimethyl.

23. A process as recited in Claim 22 wherein the second compound is N,N-dimethylanilium tetrakis(pentafluorophenyl) boronate.

24. A process as recited in Claim 1 wherein the catalyst is prepared by the following steps comprising:

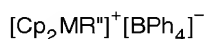
a) combining a cyclopentadienyl metal compound with a tetraphenylborate metal compound wherein the cyclopentadienyl metal compound is of the general formulae



wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, M is a Group III, IV, V or VI metal, X is a halogen and R'' is an alkyl;

b) maintaining the contact in step a) for sufficient period of time to permit abstraction of an X⁻ or a R''⁻ ion from the cyclopentadienyl metal compound by the metal of the tetraphenylborate metal compound; and

c) forming an ion pair of the general formula:

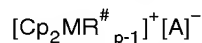


25. A catalyst system comprising:

- a) a metallocene catalyst; and
- b) an aluminum alkyl;

wherein the aluminum alkyl is of the general formula AlR_3 where R is a halogen, oxygen, hydride, alkyl, alkoxy or aryl, each R being the same or different and at least one R is an alkyl.

wherein the metallocene catalyst is an ion pair of the general formula:



wherein $[\text{Cp}_2\text{MR}^\#_{p-1}]^+$ is a metallocene cation wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, M is a Group III, IV, V or VI metal, R[#] is a hydride, a halogen, an amide or a

hydrocarbyl radical, each R* being the same or different, except when R* is a hydride, only one R* is a hydride, p is from 1 to 4 and [A]- is an anion.

26. A catalyst as recited in Claim 25 wherein R[#] is a hydrocarbyl radical selected from the group consisting of an alkyl, an aryl, an alkenyl, an alkylaryl and an arylalkyl having up to 20 carbon atoms.

27. A catalyst as recited in Claim 26 wherein R[#] is an alkyl or alkoxy of up to six carbons or an aryl of up to 10 carbons.

28. A catalyst as recited in Claim 25 wherein the M is a Group IV metal selected from the group consisting of titanium, zirconium and hafnium.

29. A catalyst as recited in Claim 25 wherein the metallocene cation is a cation of a metallocene compound chosen from the group consisting of ethylenebis(tetrahydroindenyl) zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl, ethylenebis(indenyl)hafnium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl) zirconium dimethyl.

30. A catalyst as recited in Claim 25 wherein the anion is tetrakis(pentafluorophenyl)borato anion.

31. A catalyst as recited in Claim 25 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.

32. A catalyst as recited in Claim 31 wherein the aluminum alkyl is triethylaluminum.

Patentansprüche

1. Verfahren zur Polymerisation von Olefinen, umfassend:

- a) Mischen eines Aluminiumalkyls mit einem Olefin;
- b) Herstellen eines Metallocenkatalysators;
- c) Mischen des Katalysators mit dem Aluminiumalkyl-Olefinmischung,

wobei das Aluminiumalkyl die allgemeine Formel AlR₃ aufweist, worin R ein Halogen, Sauerstoff, Hydrid, Alkyl, Alkoxy oder Aryl ist, jedes R gleich oder verschieden ist und mindestens ein R ein Alkyl ist;

wobei das Metallocen ein Ionenpaar ist, das aus einer neutralen Metallocenverbindung und einer ionisierenden ionischen Verbindung gebildet worden ist,

wobei das Ionenpaar ein Metallocenkation und ein Anion aus der ionisierenden ionischen Verbindung enthält; wobei das Anion der ionisierenden ionischen Verbindung nicht oder nur locker mit dem Metallocenkation koordiniert ist.

2. Verfahren nach Anspruch 1, wobei R ein Alkyl oder Alkoxy mit bis zu sechs Kohlenstoffatomen oder ein Aryl mit bis zu zehn Kohlenstoffatomen ist.

3. Verfahren nach Anspruch 2, wobei das molare Verhältnis von Metallocen : ionisierender Verbindung : Aluminiumalkyl von 0,5 : 1 : 0,5 bis 5 : 1 : 350 reicht.

4. Verfahren nach Anspruch 3, wobei das molare Verhältnis von Metallocen : ionisierender Verbindung : Aluminiumalkyl von 0,625 : 1 : 1,5 bis 1,5 : 1 : 77 reicht.

5. Verfahren nach Anspruch 4, wobei das molare Verhältnis von Metallocen : ionisierender Verbindung : Aluminiumalkyl 1 : 1 : 1 beträgt.

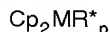
6. Verfahren nach Anspruch 5, wobei das Aluminiumalkyl aus der Gruppe ausgewählt wird, die aus Triethylaluminium und Trimethylaluminium besteht.

7. Verfahren nach Anspruch 6, wobei das Aluminiumalkyl Triethylaluminium ist.

8. Verfahren nach Anspruch 1, wobei der Katalysator durch die folgenden Schritte hergestellt wird, umfassend:

- a) Mischen einer ionisierenden ionischen Verbindung mit einem neutralen Metallocen; und
 b) Zulassen von Kontakt zwischen der ionisierenden ionischen Verbindung und dem neutralen Metallocen, um ein Ionenpaar herzustellen, bei dem das Metallocenkation als Katalysator wirkt;

wobei das neutrale Metallocen die allgemeine Formel:



aufweist, wobei Cp eine Cyclopentadienyl- oder eine substituierte Cyclopentadienylgruppe ist, wobei jedes Cp gleich oder verschieden ist, M ein Metall der Gruppen III, IV, V oder VI ist, R* ein Hydrid, ein Halogen, ein Amid oder Kohlenwasserstoffrest ist, jedes R* gleich oder verschieden ist, außer, daß nur ein R* ein Hydrid ist, wenn R* ein Hydrid ist, und p von 1 bis 4 beträgt;

wobei die ionisierende ionische Verbindung kein aktives Proton enthält und ein Carbonium-, Oxonium- oder Sulfoniumkation enthält; und

wobei das Anion der ionisierenden ionischen Verbindung mit dem Metallocenkation nicht koordiniert oder nur locker koordiniert ist und mit dem Metallocenkation chemisch nicht reagiert.

9. Verfahren nach Anspruch 8, wobei das Olefin Propylen ist.

10. Verfahren nach Anspruch 7, wobei R ein Kohlenwasserstoffrest ist, der aus der Gruppe ausgewählt wird, die aus einem Alkyl, einem Aryl, einem Alkenyl, einem Alkylaryl und einem Arylalkyl mit bis zu 20 Kohlenstoffatomen besteht.

11. Verfahren nach Anspruch 10, wobei das M ein Metall der Gruppe IV ist, das aus der Gruppe ausgewählt wird, die aus Titan, Zirkonium und Hafnium besteht.

12. Verfahren nach Anspruch 11, wobei das M Hafnium oder Zirkonium ist.

13. Verfahren nach Anspruch 12, wobei das neutrale Methylderivat eines Metallocens aus der Gruppe ausgewählt wird, die aus Ethylenbis(tetrahydroindenyl)zirkoniumdimethyl, Ethylenbis(indenyl)zirkoniumdimethyl, Ethylenbis(indenyl)hafniumdimethyl und Isopropyliden(cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl besteht.

14. Verfahren nach Anspruch 13, wobei die ionisierende ionische Verbindung Triphenylcarbeniumtetrakis(pentafluorophenyl)boronat ist.

15. Verfahren nach Anspruch 1, wobei der Katalysator durch die folgenden Schritte hergestellt wird, umfassend:

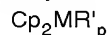
a) Kombinieren in einem geeigneten Lösungsmittel oder Verdünnungsmittel von mindestens einer ersten Verbindung, bestehend aus einem neutralen Methylderivat eines Metallocens, das mindestens einen Substituenten enthält, der dazu in der Lage ist, mit einem Proton zu reagieren, wobei das Metallocen ein Metall enthält, das aus der Gruppe ausgewählt wird, die aus Titan, Zirkonium und Hafnium besteht und mindestens einer zweiten Verbindung, die ein Kation umfaßt, das dazu in der Lage ist, ein Proton zu liefern, und ein Anion, das als das Ergebnis der Umsetzung zwischen den beiden Verbindungen gebildet wird;

b) Aufrechterhalten des Kontaktes in Schritt a) für einen ausreichenden Zeitraum, um es dem durch das Kation der zweiten Verbindung bereitgestellten Proton zu ermöglichen, mit einem Liganden der ersten Verbindung zu reagieren; und

c) Gewinnen eines aktiven Katalysators als ein direktes Produkt oder als ein Zersetzungsprodukt von einem oder mehreren der direkten Produkte von Schritt b).

16. Verfahren nach Anspruch 15, wobei das Olefin Propylen ist.

17. Verfahren nach Anspruch 16, wobei das neutrale Methylderivat eines Metallocens die allgemeine Formel:



aufweist, wobei Cp eine Cyclopentadienyl- oder eine substituierte Cyclopentadienylgruppe ist, jedes Cp gleich oder verschieden ist, M ein Metall der Gruppen III, IV, V oder VI ist, R' ein Kohlenwasserstoffrest ist, jedes R' gleich oder verschieden ist, und p von 1 bis 4 beträgt.

18. Verfahren nach Anspruch 17, wobei das M aus der Gruppe ausgewählt wird, die aus Titan, Zirkonium und Hafnium besteht.

19. Verfahren nach Anspruch 18, wobei das M Zirkonium ist.

20. Verfahren nach Anspruch 19, wobei R' aus der Gruppe ausgewählt wird, die aus einem Alkyl, einem Aryl, einem Alkenyl, einem Alkylaryl und einem Arylalkyl mit bis zu 20 Kohlenstoffatomen besteht.

21. Verfahren nach Anspruch 10, wobei das neutrale Methylderivat eines Metallocens aus der Gruppe ausgewählt wird, die aus Ethylenbis(tetrahydroindenyl)zirkoniumdimethyl und Ethylenbis(indenyl)zirkoniumdimethyl besteht.

22. Verfahren nach Anspruch 21, wobei die erste Verbindung Ethylenbis(indenyl)zirkoniumdimethyl ist.

23. Verfahren nach Anspruch 22, wobei die zweite Verbindung N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borat ist.

24. Verfahren nach Anspruch 1, wobei der Katalysator durch die folgenden Schritte hergestellt wird, umfassend:

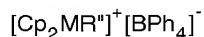
a) Kombinieren einer Cyclopentadienyl-Metallverbindung mit einer Tetraphenylborat-Metallverbindung, wobei die Cyclopentadienyl-Metallverbindung die allgemeinen Formeln



aufweisen, wobei Cp Cyclopentadienyl oder substituiertes Cyclopentadienyl ist, M ein Metall der Gruppen III, IV, V oder VI ist, X ein Halogen und R'' ein Alkyl ist;

b) Aufrechterhalten des Kontakts in Schritt a) für einen ausreichenden Zeitraum, um den Abzug eines X⁻ oder eines R''⁻ Ions aus der Cyclopentadienyl-Metallverbindung durch das Metall der Tetraphenylborat-Metallverbindung zu ermöglichen; und

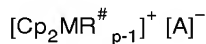
c) Bilden eines Ionenpaares der allgemeinen Formel:



25. Katalysatorsystem, umfassend:

a) einen Metallocenkatalysator; und
b) ein Aluminiumalkyl;

wobei das Aluminiumalkyl die allgemeine Formel AlR_3 aufweist, wobei R ein Halogen, Sauerstoff, Hydrid, Alkyl, Alkoxy oder Aryl ist, wobei jedes R gleich oder verschieden ist und mindestens ein R ein Alkyl ist, wobei der Metallocenkatalysator ein Ionenpaar der allgemeinen Formel



ist, wobei $[\text{Cp}_2\text{MR}^\#_{p-1}]^+$ ein Metallocenkation ist, wobei Cp Cyclopentadienyl oder substituiertes Cyclopentadienyl ist, jedes Cp gleich oder verschieden ist, M ein Metall der Gruppen III, IV, V oder VI ist, R[#] ein Hydrid, ein Halogen, ein Amid oder ein Kohlenwasserstoffrest ist, jedes R* gleich oder verschieden ist, außer daß nur ein R* ein Hydrid ist, wenn R* ein Hydrid ist, p von 1 bis 4 beträgt und $[\text{A}]^-$ ein Anion ist.

26. Katalysator nach Anspruch 25, wobei R[#] ein Kohlenwasserstoffrest ist, der aus der Gruppe ausgewählt wird, die aus einem Alkyl, einem Aryl, einem Alkenyl, einem Alkylaryl und einem Arylalkyl mit bis zu 20 Kohlenstoffatomen besteht.

27. Katalysator nach Anspruch 26, wobei R[#] ein Alkyl oder ein Alkoxy mit bis zu sechs Kohlenstoffatomen oder ein Aryl mit bis zu 10 Kohlenstoffatomen ist.

28. Katalysator nach Anspruch 25, wobei das M ein Metall der Gruppe IV ist, das aus der Gruppe ausgewählt wird, die aus Titan, Zirkonium und Hafnium besteht.

29. Katalysator nach Anspruch 25, wobei das Metallocenkation ein Kation einer Metallocenverbindung ist, die aus der Gruppe ausgewählt wird, die aus Ethylenbis(tetrahydroindenyl)zirkoniumdimethyl, Ethylenbis(indenyl)zirkoniumdimethyl, Ethylenbis(indenyl)hafniumdimethyl und Isopropyliden(cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl besteht.

30. Katalysator nach Anspruch 25, wobei das Anion ein Tetrakis(pentafluorophenyl)boratanion ist.

31. Katalysator nach Anspruch 25, wobei das Aluminiumalkyl aus der Gruppe ausgewählt wird, die aus Triethylaluminium und Trimethylaluminium besteht.

32. Katalysator nach Anspruch 31, wobei das Aluminiumalkyl Triethylaluminium ist.

Revendications

1. Procédé pour la polymérisation des oléfines comprenant :

- a) mélanger un alkylaluminium avec une oléfine;
- b) préparer un catalyseur métallocène;
- c) mélanger le catalyseur avec le mélange alkylaluminium-oléfine

dans lequel l'alkylaluminium a la formule générale AlR_3 où R est un halogène, un oxygène, un hydruure, un alkyle, un alkoxy ou un aryl, chaque R étant identique ou différent, et au moins un R étant un alkyle;
 dans lequel le métallocène est une paire d'ions formés à partir d'un composé métallocène neutre et d'un composé ionique ionisant, cette paire d'ions comprenant un cation métallocène et un anion du composé ionique ionisant;
 dans lequel l'anion du composé ionique ionisant n'est pas coordonné ou est seulement faiblement coordonné au cation métallocène.

2. Procédé selon la revendication 1 dans lequel R est un alkyle ou un alkoxy ayant jusqu'à 6 atomes de carbone ou un aryl ayant jusqu'à 10 atomes de carbone.

3. Procédé selon la revendication 2 dans lequel le rapport molaire métallocène:composé ionisant:alkylaluminium va de 0,5:1:0,5 à 5:1:350.

4. Procédé selon la revendication 3 dans lequel le rapport molaire métallocène:composé ionisant:alkylaluminium va de 0,625:1:1,5 à 1,5:1:77

5. Procédé selon la revendication 4 dans lequel le rapport molaire métallocène:composé ionisant:alkylaluminium est 1:1:1.

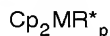
6. Procédé selon la revendication 5 dans lequel l'alkylaluminium est choisi parmi le groupe constitué du triéthylaluminium et du triméthylaluminium.

7. Procédé selon la revendication 6 dans lequel l'alkylaluminium est le triéthylaluminium.

8. Procédé selon la revendication 1 dans lequel le catalyseur est préparé suivant les étapes suivantes comprenant :

- a) mélanger un composé ionique ionisant avec un métallocène neutre; et
- b) permettre le contact entre le composé ionique ionisant et le métallocène neutre pour générer une paire d'ions dans laquelle le cation métallocène agit en tant que catalyseur;

dans lequel le métallocène neutre a la formule générale :



où Cp est un groupe cyclopentadiényle ou cyclopentadiényle substitué, chaque Cp étant identique ou différent, M est un métal du groupe III, IV, V ou VI, R^* est un hydruure, un halogène, une amine ou un radical hydrocarboné, chaque R^* étant identique ou différent, sauf si R^* est un hydruure auquel cas seulement un R^* est un hydruure, et p vaut de 1 à 4;

dans lequel le composé ionique ionisant ne contient pas de proton actif et contient un cation carbonium, oxonium ou sulfonium; et

dans lequel l'anion du composé ionique ionisant n'est pas coordonné ou est seulement faiblement coordonné au cation métallocène et est chimiquement non réactif avec le cation métallocène.

9. Procédé selon la revendication 8 dans lequel l'oléfine est le propylène.

10. Procédé selon la revendication 7 dans lequel R est un radical hydrocarboné choisi parmi le groupe constitué des alkyle, aryl, alkényl, alkylaryl ou arylalkyl ayant jusqu'à 20 atomes de carbone.

11. Procédé selon la revendication 10 dans lequel M est un métal du groupe IV choisi parmi le groupe constitué du titane, du zirconium et de l'hafnium.

12. Procédé selon la revendication 11 dans lequel M est le zirconium ou l'hafnium.

13. Procédé selon la revendication 12 dans lequel le dérivé de méthyl neutre du métallocène est choisi parmi le groupe constitué de l'éthylène bis(tétrahydroindényl)zirconium diméthyl, l'éthylènebis(indényl)hafnium diméthyl, l'éthylènebis(indényl)zirconium diméthyl et l'isopropylidène(cyclopentadiényl-1-fluorényl)zirconium diméthyl.

14. Procédé selon la revendication 13 dans lequel le composé ionique ionisant est le triphénylcarbénium tétrakis (pentafluorophényl)boronate.

15. Procédé selon la revendication 1 dans lequel le catalyseur est préparé suivant les étapes suivantes comprenant :

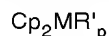
a) combiner, dans un solvant ou diluant approprié, au moins un premier composé consistant en un dérivé de méthyl neutre d'un métallocène contenant au moins un substituant capable de réagir avec un proton, le métallocène contenant un métal choisi parmi le groupe constitué du titane, du zirconium et de l'hafnium, et au moins un second composé comprenant un cation, capable de donner un proton, et un anion formés suite à la réaction entre les deux composés;

b) maintenir le contact à l'étape a) pendant une durée de temps suffisante pour permettre au proton fourni par le cation du second composé de réagir avec le ligand du premier composé; et

c) récupérer un catalyseur actif comme produit direct ou comme produit de décomposition d'un ou plusieurs des produits directs de l'étape b).

16. Procédé selon la revendication 15 dans lequel l'oléfine est le propylène.

17. Procédé selon la revendication 16 dans lequel le dérivé de méthyl neutre de métallocène a la formule générale :



où Cp est un cyclopentadiényle ou un groupe cyclopentadiényle substitué, chaque Cp étant identique ou différent, M est un métal du groupe III, IV, V ou VI, R' est un radical hydrocarboné, chaque R' étant identique ou différent, et p vaut de 1 à 4.

18. Procédé selon la revendication 17 dans lequel M est choisi parmi le groupe constitué du titane, du zirconium et de l'hafnium.

19. Procédé selon la revendication 18 dans lequel M est le zirconium.

20. Procédé selon la revendication 19 dans lequel R' est choisi parmi le groupe constitué des alkyle, aryl, alkényl, alkylaryl ou arylalkyl ayant jusqu'à 20 atomes de carbone.

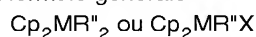
21. Procédé selon la revendication 10 dans lequel le dérivé de méthyl neutre du métallocène est choisi parmi le groupe constitué de l'éthylène bis(tétrahydroindényl)zirconium diméthyl et de l'éthylènebis(indényl)zirconium diméthyl.

22. Procédé selon la revendication 21 dans lequel le premier composé est l'éthylènebis(indényl)zirconium diméthyl.

23. Procédé selon la revendication 22 dans lequel le second composé est le N,N-diméthylanilinium tétrakis(pentafluorophényl)boronate.

24. Procédé selon la revendication 1 dans lequel le catalyseur est préparé suivant les étapes suivantes comprenant :

a) combiner un composé métal de cyclopentadiényle avec un composé métal de tétraphénylborate, où le composé métal de cyclopentadiényle a la formule générale

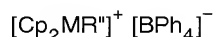


où Cp est un cyclopentadiényle ou un cyclopentadiényle substitué, M est un métal du groupe III, IV, V ou VI,

X est un halogène et R[#] est un alkyle;

b) maintenir le contact à l'étape a) pendant une durée de temps suffisante pour permettre l'abstraction d'un ion X⁻ ou R⁻ du composé métal de cyclopentadiényle par le métal du composé métal de tétraphénylborate; et

c) former une paire d'ions de formule générale :



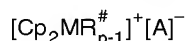
25. Système catalytique comprenant :

a) un catalyseur métallocène; et

b) un alkylaluminium;

où l'alkylaluminium a la formule générale AlR_3 où R est un halogène, un oxygène, un hydruure, un alkyle, un alkoxy ou un aryl, chaque R étant identique ou différent, et au moins un R étant un alkyle.

où le catalyseur métallocène est une paire d'ions de formule générale :



où $[\text{Cp}_2\text{MR}_{p-1}^{\#}]^+$ est un cation métallocène où Cp est un cyclopentadiényle ou un cyclopentadiényle substitué, chaque Cp étant identique ou différent, M est un métal du groupe III, IV, V ou VI, R[#] est un hydruure, un halogène, une amine ou un radical hydrocarboné, chaque R[#] étant identique ou différent, sauf si R[#] est un hydruure auquel cas seulement un R[#] est un hydruure, p vaut de 1 à 4, et $[\text{A}]^-$ est un anion.

26. Catalyseur selon la revendication 25 dans lequel R[#] est un radical hydrocarboné choisi parmi le groupe constitué des alkyle, aryl, alkényle, alkylaryl ou arylalkyl ayant jusqu'à 20 atomes de carbone.

27. Catalyseur selon la revendication 26 dans lequel R[#] est un alkyle ou un alkoxy ayant jusqu'à 6 atomes de carbone ou un aryl ayant jusqu'à 10 atomes de carbone.

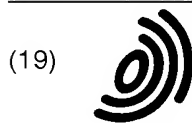
28. Catalyseur selon la revendication 25 dans lequel M est un métal du group IV choisi parmi le groupe constitué par le titane, l'hafnium et le zirconium.

29. Catalyseur selon la revendication 25 dans lequel le cation métallocène est un cation d'un composé métallocène choisi parmi le groupe constitué de l'éthylène bis(tétrahydroindényle)zirconium diméthyle, l'éthylènebis(indényle) hafnium diméthyle, l'éthylènebis(indényle)zirconium diméthyle et l'isopropylidène(cyclopentadiényle-l-fluorényle)zirconium diméthyle.

30. Catalyseur selon la revendication 25 dans lequel l'anion est l'anion tétrakis(pentafluorophényle)borate.

31. Catalyseur selon la revendication 25 dans lequel l'alkylaluminium est choisi parmi le groupe constitué du triéthylaluminium et du triméthylaluminium.

32. Catalyseur selon la revendication 31 dans lequel l'alkylaluminium est le triéthylaluminium.



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 0 426 638 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the opposition decision:
02.03.2005 Bulletin 2005/09

(51) Int Cl.⁷: **C08F 4/602**, C08F 10/00

(45) Mention of the grant of the patent:
24.04.1996 Bulletin 1996/17

(21) Application number: **90870175.8**

(22) Date of filing: **09.10.1990**

(54) **Addition of aluminium alkyl for improved metallocene catalyst**

Addition von Alkylaluminium zum Verbessern eines Metallocenkatalysators

Addition d'alkylaluminium pour un catalyseur métallocène amélioré

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: **30.10.1989 US 419222**

(43) Date of publication of application:
08.05.1991 Bulletin 1991/19

(73) Proprietor: **FINA TECHNOLOGY, INC.**
Houston, Texas 77267-4412 (US)

(72) Inventors:
• **Ewen, John A.**
Houston, Texas 77058 (US)
• **Elder, Michael J.**
Friendswood, Texas 77546 (US)

(74) Representative: **Leyder, Francis et al**
Total Petrochemicals Research Feluy
Zone Industrielle C
7181 Seneffe (Feluy) (BE)

(56) References cited:
EP-A- 0 206 794 **EP-A- 0 277 004**
US-A- 3 709 853

• **JOURNAL OF POLYMER SCIENCE/PART A:**
POLYMER CHEMISTRY, vol. 26, no. 11, October
1988, pages 3089-3102, New York, NY, US;
J.C.W. CHIEN et al.:
"Metallocene-methylaluminoxane catalysts for
olefin polymerization. I. Trimethylaluminum as
coactivator"

EP 0 426 638 B2

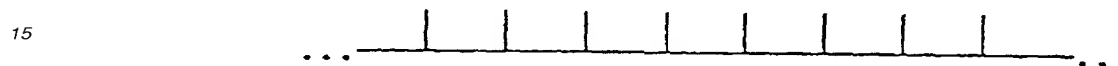
Description

FIELD OF THE INVENTION:

- 5 **[0001]** This invention relates, in general, to an improved catalyst system and, specifically, to an improved metallocene catalyst system for polymerisation of olefins by addition of an aluminum alkyl and a process for using such a catalyst.

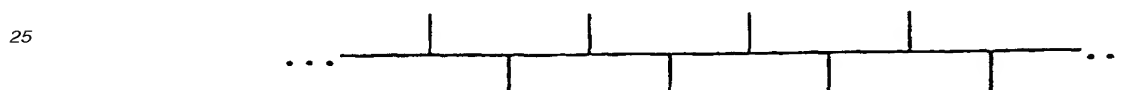
DESCRIPTION OF RELATED ART:

- 10 **[0002]** Olefins, especially propylene, may be polymerised to form polyolefins in various forms: isotactic, syndiotactic and atactic. Isotactic polypropylene contains principally repeating units with identical configurations and only a few erratic, brief inversions in the chain. Isotactic polypropylene may be structurally represented as



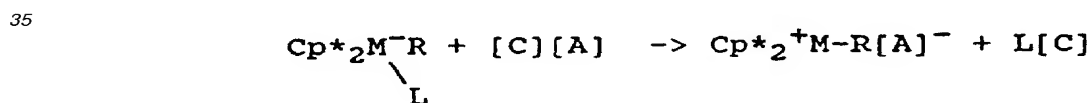
- [0003]** Isotactic polypropylene is capable of being a highly crystalline polymer with a crystalline melting point and other desirable physical properties that are considerably different from the polymer in an amorphous (noncrystalline) state.

- 20 **[0004]** A syndiotactic polymer contains principally units of exactly alternating stereo isomers and is represented by the structure:



- [0005]** A polymer chain showing no regular order of repeating unit configurations is an atactic polymer. In commercial applications, a certain percentage of atactic polymer is typically produced with the isotactic form.

- 30 **[0006]** Polymerization of olefins is primarily with Zeigler-Natta catalysts. One family of Ziegler-Natta catalysts is Group IV metallocene compounds with methylaluminoxane as a cocatalyst. It has been demonstrated that a Ziegler-Natta catalyst for olefin polymerization can be formed by combining a Group IV metallocene with an ionic compound.



40 Cp - pentamethylcyclopentadienyl

M - Group IV metal

R - alkyl

L - ligand

[C] - cation

45 [A] - anion

The resulting compound is a metallocene cation which acts as catalyst. The cation [C] of the ionic compound reacts with the metallocene to generate an ion pair. The anion, [A], is not coordinated or is only loosely coordinated with the cationic metallocene.

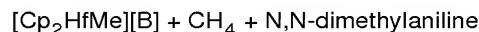
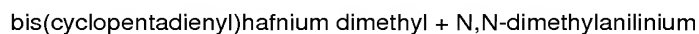
[0007] The following methods have been used to produce the above reaction:

- 50 One-Electron Oxidation - This method is illustrated in "Ethylene Polymerisation by a Cationic Dicyclopentadienylzirconium(IV) Alkyl Complex", R.F. Jordan, c.S.Bajgur, R. Willett, B. Scott, J. Am. Chem. Soc., p. 7410-7411, Vol. 108 (1986). These early examples used a Lewis base to make the metal cation less electrophilic and [BPh₄]⁻ was the anion where Ph is C₆H₅. The reaction occurred in a solvent which was coordinated with the cation. These materials were usually of low activity.

- 55 **[0008]** Protonation - This method is illustrated by "Synthesis and Insertion Reactions of Cationic Alkylbis(cyclopentadienyl) titanium Complexes", M. Bochmann, L.M.Wilson, J. Chem. Soc. Commun., p. 1610-1611, (1986); Cationic Alkylbis (cyclopentadienyl)titanium Complexes", M. Bochmann, L. Wilson, Organometallics, p. 2556-2563, Vol. 6, (1987); Insertion Reactions of Nitriles in Cationic Alkylbis(cyclopentadienyl)titanium Complexes, M. Bochmann, L. Wil-

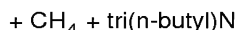
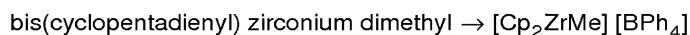
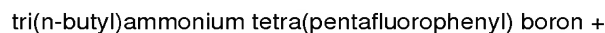
son, Organometallics, p. 1147-1154, Vol. 7 (1987).

[0009] European Patent Application 0-277-003 relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with a compound having a cation capable of donating a proton and an anion having a plurality of boron atoms. For example, the following reaction illustrates the invention:



where [B] is 7,8-dicarbaundecaborane.

[0010] European Patent Application 0-277-004 also relates to work by Turner on a catalyst prepared by a protonation method. A bis(cyclopentadienyl) metal compound is combined with an ionic compound having a cation which will irreversibly react with a ligand on the metal compound and an anion having a plurality of lipophilic radicals around a metal or metalloid ion. For example, the following reaction illustrates the invention:



[0011] A by-product of the protonation reaction is a Lewis base (amine) some of which can coordinate to the cations and thus inhibit catalyst activity. Starting materials must be chosen carefully to avoid generating particular amines which are catalyst poisons.

[0012] Carbonium Ion Chemistry - This method is illustrated by "Multiple Metal-Carbon Bonds". R R. Schrock. P R Sharp. J. Am. Chem Soc. p.2389-2399, Vol. 100, No. 8 (April, 2, 1978). A problem with both the carbonium ion chemistry method and the protonation method is that they are poisoned by basic impurities found in olefins and solvents, often resulting in runaway reactions. The high reaction temperature (over 100° C) and the short duration of the polymerisation results in short chain lengths and low molecular weight.

[0013] Metallocene catalysts are sensitive to poisons in the absence of a scavenging agent such as methylaluminoxane. Polymerisation requires high concentrations of the cations and frequently end up as either runaway reactions or yield no polymer at all.

SUMMARY OF THE INVENTION

[0014] Accordingly, it is an object of this invention to provide a process for improving metallocene catalyst activity in polymerisation of olefins.

[0015] And, it is an object of this invention to use aluminum alkyl as a scavenging agent for poisons which reduce metallocene catalyst activity.

[0016] Also, it is an object of this invention to use aluminum alkyl to improve metallocene catalyst activity of a catalyst made by the carbonium ion chemistry method.

[0017] Further, it is an object of this invention to reduce cost of a metallocene catalyst system.

[0018] Additionally, it is an object of this invention to eliminate methylaluminoxane (MAO) as a cocatalyst in polymerization of propylene.

[0019] As well, it is an object of this invention to produce a metallocene catalyst which effects a controlled polymerization of olefins without a methylaluminoxane cocatalyst.

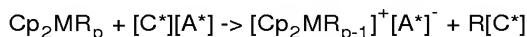
[0020] These and other objects are accomplished by mixing an aluminum alkyl with an olefin, preparing a metallocene catalyst, then mixing the catalyst with the aluminum alkyl-olefin mixture without a methylaluminoxane cocatalyst. The metallocene catalyst is an ion pair formed from a neutral metallocene compound and an ionizing compound

DESCRIPTION OF THE INVENTION

[0021] The invention is for a process of polymerizing olefins without use of a methylaluminoxane cocatalyst and for a catalyst system for use in such a process. An aluminum alkyl is mixed with an olefin and then introduced into the

presence of an ionic metallocene catalyst produced by mixing a neutral metallocene compound with an ionizing agent. Molar ratios for metallocene:ionizing compound:aluminum alkyl range from 0.5:1:0.5 to 5:1:350 and are preferably from 0.625:1:1.5 to 1.5:1:77 and are most preferably 1:1:1.

[0022] In one example of a new synthesis procedure for a metallocene catalyst, an ionizing ionic compound, such as triphenylcarbenium tetrakis(pentafluorophenyl)borate, is mixed with a neutral methyl derivatives of metallocene of the general formula Cp_2MR_p to produce the following reaction:



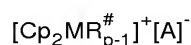
where Cp is cyclopentadienyl or substituted cyclopentadienyl. M is titanium, zirconium or hafnium, R is a hydrocarbyl radical, p is 1 to 4. C^* is a carbonium, oxonium or sulfonium cation, A^* is an anion which is not coordinated or is only loosely coordinated to the cation of the metallocene and $[C^*][A^*]$ is an ionizing agent which does not contain an active proton. Each Cp can be the same or different. Each R can be the same or different. R is preferably an alkyl, aryl, alkenyl, alkylaryl, or arylalkyl radical of up to 20 carbon atoms and is most preferably methyl. Cp_2MR_p is preferably ethylene bis(tetrahydroindenyl)zirconium dimethyl, ethylene bis(indenyl)hafnium dimethyl, ethylene bis(indenyl)zirconium dimethyl or isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl and most preferably ethylenebis(indenyl)zirconium dimethyl. Each reactant is placed in a solvent which is not coordinated or is only loosely coordinated with the metallocene cation, such as methylene chloride or toluene. The preferred solvent is toluene.

[0023] The two reactants dissolved separately in the same solvents are mixed together at room temperature. The ionizing compound ionizes the metallocene and an ion pair is formed in which the metallocene cation acts as a catalyst. After mixing, the mixture is added to an olefin under conditions to effect polymerization. The olefin is preferably propylene. This procedure is covered by European Patent Application No. 90870174.1 which is hereby incorporated by reference into this application.

[0024] In another example of a synthesis procedure for a catalyst, a neutral derivative of a metallocene, such as a cyclopentadienyl metal compound, is combined with a tetraphenylborate metal compound. The neutral metallocene compound is of the general formula $Cp_2MR''_2$, where Cp is cyclopentadienyl or substituted cyclopentadienyl, M is titanium, zirconium or hafnium and R'' is an alkyl. An R^+ is abstracted from the metallocene by the metal of the tetraphenylborate metal compound, resulting in an ion pair of the general formula $[Cp_2MR'']^+ [BPh_4]^-$ where BPh_4 is a tetraphenyl borate anion.

[0025] An aluminum alkyl is mixed with an olefin and brought to reaction temperature. The aluminum alkyl is of the general formula AlR_3 where R is a halogen, oxygen, hydride, alkylalkoxy or aryl, each R being the same or different and at least one R is an alkyl. The aluminum alkyl is preferably trimethylaluminum (TMA) or triethylaluminum (TEA1) and is most preferably triethylaluminum. The olefin is any of the olefins but is preferably propylene or ethylene and is most preferably propylene. The mixture of aluminum alkyl and olefin is brought in contact with a metallocene catalyst. The catalyst may be made by any known method, including but not limited to those described above.

[0026] The catalyst system is an ionic metallocene catalyst of the general formula:



wherein $[Cp_2MR_{p-1}^{\#}]^+$ is a metallocene cation wherein Cp is cyclopentadienyl or substituted cyclopentadienyl, each Cp being the same or different, $R^{\#}$ is a hydrocarbyl radical, each $R^{\#}$ being the same or different, p is from 1 to 4 and $[A]^-$ is an anion. $R^{\#}$ is preferably a hydrocarbyl radical, such as an alkyl, an aryl, an alkenyl, an alkylaryl or an arylalkyl having up to 20 carbon atoms and is most preferably an alkyl or alkoxy of up to six carbon atoms or an aryl of up to 10 carbon atoms. M is titanium, zirconium and hafnium and is most preferably zirconium or hafnium. The metallocene cation is preferably a cation of ethylenebis(tetrahydroindenyl)zirconium dimethyl, ethylenebis(indenyl)zirconium dimethyl, ethylenebis(indenyl)hafnium dimethyl and isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl and is most preferably ethylenebis(tetrahydroindenyl)zirconium dimethyl. The anion is preferably tetrakis(pentafluorophenyl)borate. The aluminum is as described above and is most preferably TMA or TEA1 and is most preferably TEA1.

[0027] The following metallocene-ionizing agent systems were evaluated with and without addition of an aluminum alkyl:

1. $Et(Ind)_2ZrMe_2/[Ph_3C][BPh^*_4]$
2. $Et(Ind)_2HfMe_2/[Ph_3C][BPh^*_4]$
3. $Et(Ind)_2ZrMe_2/[Me_2PhN][BPh^*_4]$ (outside the claimed invention)
4. $iPr(Cp^1-Flu)ZrMe_2/[Ph_3C][BPh^*_4]$
5. $Et(H_4Ind)_2ZrMe_2/[Ph_3C][BPh^*_4]$

6. $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2/[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$ (outside the claimed invention)

$\text{Et}(\text{Ind})_2\text{ZrMe}_2$ is ethylene bis(indenyl)zirconium dimethyl, $\text{iPr}(\text{Cp-1-Flu})\text{ZrMe}_2$ is isopropylidene (cyclopentadienyl-1-fluorenyl)zirconium dimethyl, $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$ is ethylene bis(tetrahydroindenyl)zirconium dimethyl, $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$ is triphenylcarbenium tetrakis(pentafluorophenyl)boronate, $(\text{Me}_2\text{PhN})[\text{BPh}^*_4]$ is N,N-dimethylanilinium tetrakis(pentafluorophenyl)boronate.

[0028] The invention having been generally described, the following examples are given as particular embodiments of the invention and to demonstrate the practice and advantages thereof. It is understood that the examples are given by way of illustration and are not intended to limit the specification or the claims to follow in any manner.

GROUP 1:

EXAMPLE I

[0029] 100 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 10 ml of toluene. 60 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ was dissolved in 10 ml of toluene. The two solutions were mixed together for 5 minutes at room temperature.

[0030] Reactor temperature was set to 50°C and one liter of propylene was pumped into the reactor. The catalyst mixture was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 50°C and the contents of the reactor were agitated for sixty minutes. At the end of the polymerization, the reactor is cooled and the unreacted propylene was vented from the reactor.

[0031] The reaction product was dried under vacuum at approximately 40°C for 12 hours. The polymer was then weighed and analysed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

EXAMPLE II

[0032] The procedure of Example 1 was repeated with the contents of the reactor being agitated for 30 minutes. The results are shown in Table I.

EXAMPLE III

[0033] The procedure of Example 1 was repeated with the contents of the reactor set point temperature being set at 70°C. The results are shown in Table I.

EXAMPLE IV

[0034] 0.32 mmol of trimethylaluminum (TMA) was dissolved in 5 ml of toluene and was added to a 2 liter Zipperclave reactor under 5 psig of nitrogen. Reactor temperature was set to 70°C and one liter of propylene was pumped into the reactor. The mixture was stirred for ten minutes at 1200 rpm.

[0035] 100 mg of triphenylcarbenium tetrakis(pentafluorophenyl) boronate was dissolved in 10 ml of toluene. 60 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ was dissolved in 10 ml of toluene. The two solutions were mixed together for 5 minutes at room temperature.

[0036] The catalyst mixture was added to a 40 ml stainless steel bomb equipped with ball valves on each end. 400 ml of propylene was pumped through the bomb into the reactor. The reactor temperature remained at 70°C and the contents of the reactor were agitated for sixty minutes. At the end of the polymerization, the reactor is cooled and the unreacted propylene was vented from the reactor.

[0037] The reaction product was dried under vacuum at approximately 40°C for 12 hours. The polymer was then weighed and analyzed for melting point. The melting point was derived from differential scanning calorimetry (DSC). The results are shown in Table I.

EXAMPLE V

[0038] The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1) and agitating the contents of the reactor for 10 minutes. The results are shown in Table I.

EXAMPLE VI

[0039] The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 50 mg of triphenyl-carbenium tetrakis(pentafluorophenyl) boronate and 30 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for 5 minutes. The results are shown in Table I.

EXAMPLE VII

[0040] The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 16 mg of triphenyl-carbenium tetrakis(pentafluorophenyl)boronate and 10 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for ten minutes. The results are shown in Table I.

EXAMPLE VIII

[0041] The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenyl-carbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for sixty minutes. The results are shown in Table I.

EXAMPLE IX

[0042] The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenyl-carbenium tetrakis(pentafluorophenyl)boronate and 1.25 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for sixty minutes. The results are shown in Table I.

EXAMPLE X

[0043] The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenyl-carbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE XI

[0044] The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 8 mg of triphenyl-carbenium tetrakis(pentafluorophenyl)boronate and 2.5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for forty minutes. The results are shown in Table I.

EXAMPLE XII

[0045] The procedure of Example II was repeated using 0.33 mmol of triethylaluminum (TEA1), 8 mg of triphenyl-carbenium tetrakis(pentafluorophenyl)boronate and 5 mg of Et(Ind)₂ZrMe₂. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE XIII

[0046] The procedure of Example II was repeated with 5 mg of Et(Ind)₂ZrMe₂, 8 mg of [Ph₃C][BPh*₄], 0.66 mmol of triethyl aluminum and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XIV

[0047] The procedure of Example II was repeated with 2.5 mg of Et(Ind)₂ZrMe₂, 8 mg of [Ph₃C][BPh*₄], 0.66 mmol of triethyl aluminum and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XV

[0048] The procedure of Example II was repeated with 2.5 mg of Et(Ind)₂ZrMe₂, 4 mg of [Ph₃C][BPh*₄], 0.66 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XVI

[0049] The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 4 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.99 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XVII

[0050] The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 24 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.66 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

EXAMPLE XVIII

[0051] The procedure of Example II was repeated with 2.5 mg $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 24 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 2.00 mmol of TEA1 and a run time of 30 minutes. The results are shown in Table I.

GROUP 2:

EXAMPLE XIX

[0052] The procedure of Example II was repeated with 20 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 80 mg of $[\text{Ph}_3\text{C}][\text{BPh}^*_4]$, 0.42 mmol of trimethyl aluminum and a run time of 30 minutes. The results are shown in Table I

GROUP 3: (outside claimed invention)

EXAMPLE XX

[0053] The procedure of Example 1 was repeated with 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 7 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXI

[0054] The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 7.0 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, 0.66 mmol triethyl aluminum and a run time of 5 minutes. The results are shown in Table I

EXAMPLE XXII

[0055] The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 7.0 mg of N, N-dimethylanilinium tetrakis(pentafluorophenyl)boronate and 2.5 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for twenty-five minutes. The results are shown in Table I.

EXAMPLE XXIII

[0056] The procedure of Example II was repeated using 0.66 mmol of triethylaluminum (TEA1), 3.5 mg of N,N-dimethylanilinium tetrakis(pentafluorophenyl)boronate and 1.25 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$. The contents of the reactor were agitated for thirty minutes. The results are shown in Table I.

EXAMPLE XXIV

[0057] The procedure of Example II was repeated with 1.25 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 3.5 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, 0.66 mmol of triethylaluminum and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXV

[0058] The procedure of Example II was repeated with 0.625 mg of $\text{Et}(\text{Ind})_2\text{ZrMe}_2$, 1.75 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$, 0.66 mmol of triethylaluminum and a run time of 60 minutes. The results are shown in Table I.

GROUP 4:

EXAMPLE XXVI

- 5 **[0059]** The procedure of Example I was repeated with 40 mg of $iPr(Cp-1-Flu)ZrMe_2$, 60 mg of $[Ph_3C][BPh^*_4]$ and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXVII

- 10 **[0060]** The procedure of Example I was repeated with 60 mg of $iPr(Cp-1-Flu)ZrMe_2$ 100 mg of $[Ph_3C][BPh^*_4]$. and a run time of 60 minutes The results are shown in Table I

EXAMPLE XXVIII

- 15 **[0061]** The procedure of Example II was repeated with 60 mg of $iPr(Cp-1-Flu)ZrMe_2$ 100 mg of $[Ph_3C][BPh^*_4]$ 0.16 mmol of trimethylaluminum and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXIX

- 20 **[0062]** The procedure of Example II was repeated using 0.48 mmol of trimethylaluminum (TMA). 100 mg of $[Ph_3C][BPh^*_4]$ and 60 mg of $iPr(Cp-1-flu)ZrMe_2$, and a run time of 60 minutes. The results are shown in Table I.

EXAMPLE XXX

- 25 **[0063]** The procedure of Example II was repeated with 20 mg of $iPr(Cp-1-Flu)ZrMe_2$. 60 mg of $[Ph_3C][BPh^*_4]$ 0.16 mmol of trimethylaluminum and a run time of 60 minutes. The results are shown in Table I.

GROUP 5:

30 EXAMPLE XXXI

- [0064]** The procedure of Example 1 was repeated with 15 mg of $Et(H_4Ind)_2ZrMe_2$. 30 mg of $[Ph_3C][BPh^*_4]$. and a run time of 60 minutes. The results are shown in Table I.

35 EXAMPLE XXXII

- [0065]** The procedure of Example 1 was repeated with 20 mg of $Et(H_4Ind)_2ZrMe_2$, 40 mg of $[Ph_3C][BPh^*_4]$, and a run time of 60 minutes. The results are shown in Table I.

40 EXAMPLE XXXIII

- [0066]** The procedure of Example 1 was repeated with 20 mg of $Et(H_4Ind)_2ZrMe_2$. 40 mg of $[Ph_3C][BPh^*_4]$, and a run time of 5 minutes. The results are shown in Table I.

45 EXAMPLE XXXIV

- [0067]** The procedure of Example II was repeated with 2.5 mg of $Et(H_4Ind)_2ZrMe_2$ 8 mg of $[Ph_3C][BPh^*_4]$, 0.66 mmol of TEA1 and a run time of 60 minutes. The results are shown in Table I.

50 GROUP 6: (outside claimed invention)

EXAMPLE XXXV

- 55 **[0068]** The procedure of Example 1 was repeated with 50 mg of $Et(H_4Ind)_2ZrMe_2$, 40 mg of $[Me_2PhN][BPh^*_4]$, and a run time of 120 minutes. The results are shown in Table I.

EXAMPLE XXXVI

[0069] The procedure of Example II was repeated with 2.5 mg of $\text{Et}(\text{H}_4\text{Ind})_2\text{ZrMe}_2$, 9.2 mg of $[\text{Me}_2\text{PhN}][\text{BPh}^*_4]$ 0.66 mmol of TEA1 and a run time of 60 minutes. The results are shown in Table I.

[0070] The following results are from the experimental runs described above using the method of the present invention.

TABLE I

10

Run #	Catalyst umol (mg)	Ionizing Agent umol (mg)	Al-alkyl mmol	Run Time min.
	Et(Ind) ₂ ZrMe ₂	[Ph ₃ C][BPh* ₄]		
15	1 159(60)	109(100)	0	60
	2 159(60)	109(100)	0	30
	3 159(60)	109(100)	0	60
	4 159(60)	109(100)	TMA 0.32	60
	5 159(60)	109(100)	TEA1 0.33	10
	6 80(30)	54(50)	0.33	5
20	7 26.5(10)	17.3(16)	0.33	10
	8 6.63(2.5)	8.64(8)	0.66	60
	9 3.36(1.25)	8.64(8)	0.66	60
	10 6.63(2.5)	8.64(8)	0.66	30
	11 6.63(2.5)	8.64(8)	0.66	40
25	12 13.3(5)	8.6(8)	0.33	30
	13 13.3(5)	8.64(8)	0.66	30
	14 6.63(2.5)	8.64(8)	0.66	60
	15 6.63(2.5)	4.3(4)	0.66	30
	16 6.63(2.5)	4.3(4)	0.99	30
	17 6.63(2.5)	26(24)	0.66	30
30	18 6.63(2.5)	26(24)	2.00	30
	Et(Ind) ₂ HfMe ₂	[Ph ₃ C][BPh* ₄]		
	19 53(20)	85(80)	TMA 0.42	30
	Et(Ind) ₂ ZrMe ₂	[Me ₂ PhN][BPh* ₄]		
35	20 6.6(2.5)	8.7(7.0)	0	60
	21 6.6(2.5)	8.7(7.0)	TEA1 0.66	5
	22 6.6(2.5)	8.7(7.0)	0.66	25
	23 3.3(1.25)	4.35(3.5)	0.66	30
	24 3.3(1.25)	4.35(3.5)	0.66	60
40	25 1.65(.0625)	2.175(1.75)	0.66	60
	iPr(Cp-1-Flu)ZrMe ₂	[Ph ₃ C][BPh* ₄]		
	26 102(40)	65(60)	0	60
	27 154(60)	109(100)	0	60
	28 154(60)	109(100)	TMA 0.16	60
45	29 154(60)	109(100)	0.48	60
	30 51(20)	65(60)	0.16	60
	Et(H ₄ Ind) ₂ ZrMe ₂	[Ph ₃ C][BPh* ₄]		
	31 40(15)	33(30)	0	60
	32 53(20)	44(40)	0	60
50	33 80(30)	67(60)	0	5
	34 7(2.5)	8.8(8.0)	TEA1 0.66	60
	Et(H ₄ Ind) ₂ ZrMe ₂	[Me ₂ PhN][BPh* ₄]		
	35 133(50)	44(40)	0	120
	36 7(2.5)	10(9.2)	TEA1 0.66	60

Run #	Polymeri- zation Temp (°C)	Yield (gms)	Melting Temp (°C)
1	50	19	137
2	50	11	125
3	70	8	126
4	70	270	124
5	70*	340	126
6	70*	432	No Melt
7	70*	260	118
8	70	319	129
9	70	89	132
10	70	117	
11	70*	377	131
12	70	22	132
13	70	51	131
14	70*	357	127
15	70	9	132
16	70	11	134
17	70	149	131
18	70	62	130
19	70	51	131
20	70	-	-
21	70*	106	125
22	70*	405	127
23	70*	434	127
24	70	385	131
25	70	253	131
26	80	2	-
27	70	51	-
28	70*	284	116
29	70*	268	117
30	70*	156	116
31	50	2	142
32	50	35	138
33	120	70	127
34	70	154	115
35	50	50	133
36	70	116	116

*Exotherm; reaction temperature increased by more than 10°C.

[0071] The process described by this invention synthesizes cations which are used as catalysts in olefin polymerization. The process of making catalysts with this invention produces catalysts having high activity and reduces the by-products which can inhibit catalyst activity. This new synthesis also reduces the catalyst poisons found in the solvents which can inhibit catalyst activity.

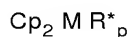
[0072] The addition of an aluminum alkyl to ionic metallocene catalyst systems was found to result in reproducible, controllable, high efficiency polymerizations. The addition of an alkyl aluminum provides a scavenging agent for catalyst poisons. The quantity of aluminum alkyl added is relatively small and aluminum alkyls are relatively inexpensive. The metallocene cation/aluminum alkyl combination results in a better catalyst system than the cations alone and give consistently high activities.

Claims

1. A process for polymerization of olefins comprising :

- mixing an aluminum alkyl with an olefin;
- preparing a metallocene catalyst;
- mixing the catalyst with the aluminium alkyl-olefin mixture ;

wherein the aluminum alkyl is of the general formula AlR'_3 wherein R' is an alkyl of up to six carbon atoms ;
 wherein the metallocene catalyst is an ion pair formed from a neutral metallocene compound and an ionizing
 ionic compound and comprises a metallocene cation and an anion from the ionizing ionic compound;
 wherein ionizing ionic compound does not contain an active proton and is of the general formula $[\text{C}][\text{A}]$,
 5 wherein $[\text{C}]$ contains a carbonium, oxonium or sulfonium cation and the anion $[\text{A}]$ is not coordinated or is only
 loosely coordinated to the metallocene cation; and
 wherein the neutral metallocene is of the general formula



wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or differ-
 ent, R^* is a hydrocarbyl radical, R^* being the same or different,

M is titanium, zirconium or hafnium, p is 1 to 4 ;

excluding the process wherein

(i) the aluminium alkyl is trimethylaluminium ; and

(ii) the olefin is propylene; and

(iii) the neutral metallocene compound is isopropylidene (cyclopentadienyl-1-fluorenyl) zirconium dimethyl ;
 and

(iv) the ionic ionizing compound is triphenylcarbenium tetrakis (pentafluorophenyl) boronate.

2. A process as recited in claim 1 wherein R^* is an alkyl, aryl, alkenyl, alkylaryl, or arylalkyl radical of up to 20 carbon
 atoms.

3. A process as recited in claim 1 wherein the molar ratio for metallocene: ionizing compound: aluminum alkyl ranges
 from 0.5:1:0.5 to 5:1:350.

4. A process as recited in claim 3 wherein the molar ratio for metallocene: ionizing compound: aluminum alkyl ranges
 from 0.625:1:1.5 to 1.5:1:77.

5. A process as recited in claim 4 wherein the molar ratio for metallocene: ionizing compound: aluminum alkyl is 1:1:1.

6. A process as recited in claim 1 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum
 and trimethylaluminum.

7. A process as recited in claim 6 wherein the aluminum alkyl is triethylaluminum.

8. A process as recited in claim 1 wherein the olefin is propylene.

9. A process as recited in claim 1 wherein M is selected from the group consisting of zirconium and hafnium.

10. A process as recited in claim 1 wherein the neutral metallocene is chosen from the group consisting of ethylenebis
 (tetrahydroindenyl) zirconium dimethyl, ethylenebis(indenyl) zirconium dimethyl, ethylenebis(indenyl) hafnium
 dimethyl, and isopropylidene(cyclopentadienyl-1-fluorenyl) zirconium dimethyl.

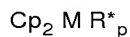
11. A process as recited in claim 1 wherein the ionic ionizing compound is triphenylcarbenium tetrakis(pentafluoroph-
 enyl) boronate.

12. A process as recited in claim 1 wherein wherein the catalyst is prepared by the following steps comprising:

a) mixing an ionizing ionic compound with a neutral metallocene; and

b) allowing contact between the ionizing ionic compound and the neutral metallocene to generate an ion pair
 in which the metallocene cation acts as a catalyst:

wherein the neutral metallocene is of the general formula

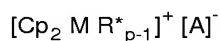


wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group each Cp being the same or different, R* is a hydrocarbyl radical, R* being the same or different, M is titanium, zirconium or hafnium, p is 1 to 4; wherein ionizing ionic agent does not contain an active proton and contains a carbonium, oxonium or sulfonium cation and wherein the anion of the ionizing ionic compound is not coordinated or is only loosely coordinated to the metallocene cation and is chemically unreactive with the metallocene cation.

13. A catalyst system comprising:

- a) a metallocene catalyst, and
- b) an aluminum alkyl

wherein the aluminum alkyl is of the general formula AlR'_3 wherein R' is an alkyl having up to 6 carbon atoms, wherein the metallocenecatalyst is an ion pair of the general formula:



wherein $[\text{Cp}_2 \text{M R}^*_{\text{p-1}}]^+$ is a metallocene cation wherein Cp is a cyclopentadienyl or a substituted cyclopentadienyl group, each Cp being the same or different, R* is a hydrocarbyl radical, R* being the same or different, M is titanium, zirconium or hafnium, p is 1 to 4 ;

wherein the metallocene is an ion pair formed from a neutral metallocene compound and an ionizing ionic compound said ion pair comprising a metallocene cation and an anion from the ionizing compound;

wherein the ionizing ionic compound does not contain an active proton and is of the formula $[\text{C}] [\text{A}]$, wherein C contains a carbonium, oxonium or sulfonium cation, and wherein the anion A is not coordinated or is loosely coordinated to the metallocene cation;

excluding the catalyst system wherein

- (i) the aluminium alkyl is trimethylaluminium ; and
- (ii) the neutral metallocene compound is isopropylidene (cyclopentadienyl-1-fluorenyl) zirconium dimethyl ; and
- (iii) the ionic ionizing compound is triphenylcarbenium tetrakis (pentafluorophenyl) boronate.

14. A catalyst system as recited in claim 13 wherein R* is an alkyl, aryl, alkenyl, alkylaryl, or arylalkyl radical of up to 20 carbon atoms.

15. A catalyst system as recited in claim 13 wherein R* is an alkyl having up to six carbon atoms or an aryl having up to 10 carbon atoms.

16. A catalyst system as recited in claim 13 wherein the aluminum alkyl is selected from the group consisting of triethylaluminum and trimethylaluminum.

17. A catalyst system as recited in claim 16 wherein the aluminum alkyl is triethylaluminum.

18. A catalyst system as recited in claim 13 wherein the neutral metallocene is chosen from the group consisting of ethylenebis(tetrahydroindenyl) zirconium dimethyl, ethylenebis(indenyl) zirconium dimethyl, ethylenebis(indenyl) hafnium dimethyl, and isopropylidene(cyclopentadienyl-1-fluorenyl) zirconium dimethyl.

19. A catalyst system as recited in claim 13 wherein the anion is tetrakis(pentafluorophenyl) borato anion.

Patentansprüche

1. Verfahren zur Polymerisation von Olefinen, umfassend :

- a) Mischen eines Aluminiumalkyls mit einem Olefin;
- b) Herstellen eines Metallocenkatalysators;
- c) Mischen des Katalysators mit dem Aluminiumalkyl-Olefingemisch;

5 wobei das Aluminiumalkyl die allgemeine Formel AlR'_3 aufweist, worin R' ein Alkyl von bis zu sechs Kohlenstoffatomen ist;
 wobei der Metallocenkatalysator ein Ionenpaar ist, das aus einer neutralen Metallocenverbindung und einer ionisierenden ionischen Verbindung gebildet worden ist und ein Metallocenkation und ein Anion aus der ionisierenden ionischen Verbindung enthält;
 10 wobei die ionisierende ionische Verbindung kein aktives Proton enthält und die allgemeine Formel $[\text{C}] [\text{A}]$ hat, wobei $[\text{C}]$ ein Carbonium-, Oxonium- oder Sulfoniumkation enthält und das Anion $[\text{A}]$ mit dem Metallocenkation nicht koordiniert ist oder nur locker koordiniert ist; und
 wobei das neutrale Metallocen die allgemeine Formel



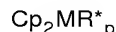
aufweist, wobei Cp eine Cyclopentadienyl- oder eine substituierte Cyclopentadienylgruppe ist, wobei jedes Cp gleich oder verschieden ist, R^* ein Kohlenwasserstoffrest ist, wobei R^* gleich oder verschieden ist, M Titanium, Zirkonium oder Hafnium ist, p 1 bis 4 ist, ausschließlich des Verfahrens, worin

- 20 (i) das Aluminiumalkyl Trimethylaluminium ist; und
 (ii) das Olefin Propylen ist; und
 (iii) die neutrale Metallocenverbindung Isopropyliden (Cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl ist; und
 25 (iv) die ionische ionisierende Verbindung Triphenylcarbeniumtetrakis(pentafluorphenyl)boronat ist.

2. Verfahren gemäß Anspruch 1, wobei R' ein Alkyl-, Aryl-, Alkenyl-, Alkylaryl- oder Arylalkylradikal von bis zu 20 Kohlenstoffatomen ist.
- 30 3. Verfahren gemäß Anspruch 1, wobei das Molverhältnis für Metallocen : ionisierender Verbindung : Aluminiumalkyl sich von 0,5 : 1 : 0,5 bis auf 5 : 1 : 350 beläuft.
4. Verfahren gemäß Anspruch 3, wobei das Molverhältnis für Metallocen : ionisierender Verbindung : Aluminiumalkyl sich von 0,625 : 1 : 1,5 bis auf 1,5 : 1 : 77 beläuft.
- 35 5. Verfahren gemäß Anspruch 4, wobei das Molverhältnis für Metallocen : ionisierender Verbindung : Aluminiumalkyl 1 : 1 : 1 ist.
6. Verfahren gemäß Anspruch 1, wobei das Aluminiumalkyl aus der aus Triethylaluminium und Trimethylaluminium bestehenden Gruppe gewählt ist.
- 40 7. Verfahren gemäß Anspruch 6, wobei das Aluminiumalkyl Triethylaluminium ist.
8. Verfahren gemäß Anspruch 1, wobei das Olefin Propylen ist.
- 45 9. Verfahren gemäß Anspruch 1, wobei M aus der aus Zirkonium und Hafnium bestehenden Gruppe gewählt ist.
10. Verfahren gemäß Anspruch 1, wobei das neutrale Metallocen aus der aus Ethylenbis(tetrahydroindenyl)zirkoniumdimethyl, Ethylenbis(indenyl)zirkoniumdimethyl, Ethylenbis(indenyl)hafniumdimethyl und Isopropyliden(cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl bestehenden Gruppe gewählt ist.
- 50 11. Verfahren gemäß Anspruch 1, wobei die ionische ionisierende Verbindung Triphenylcarbeniumtetrakis(pentafluorphenyl)boronat ist.
- 55 12. Verfahren gemäß Anspruch 1, wobei der Katalysator durch die folgenden Schritte hergestellt wird, umfassend
 - a) Mischen einer ionisierenden ionischen Verbindung mit einem neutralen Metallocen; und
 - b) Zulassen von Kontakt zwischen der ionisierenden ionischen Verbindung und dem neutralen Metallocen, um

ein Ionenpaar herzustellen, bei dem das Metallocenkation als Katalysator wirkt;

wobei das neutrale Metallocen die allgemeine Formel



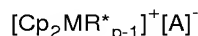
aufweist, wobei Cp eine Cyclopentadienyl- oder eine substituierte Cyclopentadienylgruppe ist, wobei jedes Cp gleich oder verschieden ist, R* ein Hydrocarbylradikal ist, wobei R* gleich oder verschieden ist, M Titanium, Zirkonium oder Hafnium ist, p 1 bis 4 ist, wobei das ionisierende ionische Mittel kein aktives Proton enthält und ein Carbonium-, Oxonium- oder Sulfoniumkation enthält; und wobei das Anion der ionisierenden ionischen Verbindung mit dem Metallocenkation nicht koordiniert oder nur locker koordiniert ist und mit dem Metallocenkation chemisch nicht reagiert.

13. Ein Katalysatorsystem, umfassend :

- a) einen Metallocenkatalysator, und
- b) ein Aluminiummalkyl,

wobei das Aluminiummalkyl die allgemeine Formel AlR'_3 aufweist, wobei R' ein Alkyl mit bis zu 6 Kohlenstoffatomen ist,

wobei der Metallocenkatalysator ein Ionenpaar mit der allgemeinen Formel



ist, wobei $[\text{Cp}_2\text{MR}^*_{p-1}]^+$ ein Metallocenkation ist, wobei Cp eine Cyclopentadienyl- oder substituierte Cyclopentadienylgruppe ist, wobei jedes Cp gleich oder verschieden ist, R* ein Kohlenwasserstoffrest ist, wobei R* gleich oder verschieden ist, M Titanium, Zirkonium oder Hafnium ist, p 1 bis 4 ist, wobei das Metallocen ein aus einer neutralen Metallocenverbindung und einer ionisierenden ionischen Verbindung gebildetes Ionenpaar ist, wobei besagtes Ionenpaar ein Metallocenkation und ein Anion aus der ionisierenden Verbindung umfasst;

wobei die ionisierende ionische Verbindung kein aktives Proton enthält und die Formel $[\text{C}][\text{A}]$ aufweist, wobei C ein Carbonium-, Oxonium- oder Sulfoniumkation enthält und wobei das Anion mit dem Metallocenkation nicht koordiniert ist oder locker koordiniert ist; ausschließlich des Katalysatorsystems, wobei

- (i) das Aluminiummalkyl Trimethylaluminium ist; und
- (ii) die neutrale Metallocenverbindung Isopropyliden (cyclopentadienyl-1-fluorenyl) zirkoniumdimethyl ist; und
- (iii) die ionische ionisierende Verbindung Triphenylcarbeniumtetrakis(pentafluorophenyl)-boronat ist.

14. Katalysatorsystem gemäß Anspruch 13, wobei R* ein Alkyl-, Aryl-, Alkenyl-, Alkylaryl- oder Arylalkylradikal von bis zu 20 Kohlenstoffatomen ist.

15. Katalysatorsystem gemäß Anspruch 13, wobei R* ein Alkyl mit bis zu sechs Kohlenstoffatomen oder ein Aryl mit bis zu 10 Kohlenstoffatomen ist.

16. Katalysatorsystem gemäß Anspruch 13, wobei das Aluminiummalkyl aus der aus Triethylaluminium und Trimethylaluminium bestehenden Gruppe gewählt ist.

17. Katalysatorsystem gemäß Anspruch 16, wobei das Aluminiummalkyl Triethylaluminium ist.

18. Katalysatorsystem gemäß Anspruch 13, wobei das neutrale Metallocen aus der aus Ethylenbis(tetrahydroindenyl) zirkoniumdimethyl, Ethylenbis(indenyl)zirkoniumdimethyl, Ethylenbis(indenyl)hafniumdimethyl und Isopropyliden (cyclopentadienyl-1-fluorenyl)zirkoniumdimethyl bestehenden Gruppe gewählt ist.

19. Katalysatorsystem gemäß Anspruch 13, wobei das Anion ein Tetrakis(pentafluorophenyl)boratanion ist.

Revendications

1. Procédé pour la polymérisation d'oléfines comprenant le fait de :

- 5 a) mélanger un alkylaluminium avec une oléfine ;
 b) préparer un catalyseur du type d'un métallocène ;
 c) mélanger le catalyseur avec le mélange alkylaluminium-oléfine ;

10 dans lequel l'alkylaluminium répond à la formule générale AlR'_3 où R' représente un groupe alkyle contenant jusqu'à six atomes de carbone ;

 dans lequel le catalyseur du type d'un métallocène représente une paire d'ions formée à partir d'un composé de métallocène neutre et d'un composé ionique ionisant et comprend un cation de métallocène et un anion provenant du composé ionique ionisant ;

15 dans lequel le composé ionique ionisant ne contient pas un proton actif et répond à la formule générale $[C][A]$ où $[C]$ contient un cation carbonium, un cation oxonium ou un cation sulfonium et l'anion $[A]$ n'est pas coordonné ou est coordonné seulement de manière lâche au cation de métallocène ; et

 dans lequel le métallocène neutre répond à la formule générale



20 où Cp représente un groupe cyclopentadiényle ou un groupe cyclopentadiényle substitué, chaque groupe Cp étant identique ou différent, R^* représente un radical hydrocarbyle, les radicaux R^* étant identiques ou différents, M représente le titane, le zirconium ou le hafnium, p est égal à 1 - 4 ;

25 à l'exclusion du procédé dans lequel

- (i) l'alkylaluminium est le triméthylaluminium ;
 (ii) l'oléfine est le propylène ; et
 (iii) le composé de métallocène neutre est le diméthyl isopropylidène (cyclopentadiényl-1-fluorényl) zirconium ;
 et
 (iv) le composé ionique ionisant est le tétrakis (pentafluorophényl) borate de triphénylcarbénium.

30 2. Procédé selon la revendication 1, dans lequel R^* représente un groupe alkyle, un groupe aryle, un groupe alcényle, un groupe alkylaryle ou un groupe arylalkyle contenant jusqu'à 20 atomes de carbone.

35 3. Procédé selon la revendication 1, dans lequel le rapport molaire métallocène : composé ionisant : alkylaluminium se situe dans la plage de 0,5 : 1 : 0,5 à 5 : 1 : 350.

40 4. Procédé selon la revendication 3, dans lequel le rapport molaire métallocène : composé ionisant : alkylaluminium se situe dans la plage de 0,625 : 1 : 1,5 à 1,5 : 1 : 77.

 5. Procédé selon la revendication 4, dans lequel le rapport molaire métallocène : composé ionisant : alkylaluminium se situe dans la plage de 1 : 1 : 1.

45 6. Procédé selon la revendication 1, dans lequel l'alkylaluminium est choisi parmi le groupe constitué par le triéthylaluminium et le triméthylaluminium.

 7. Procédé selon la revendication 6, dans lequel l'alkylaluminium est le triéthylaluminium.

50 8. Procédé selon la revendication 1, dans lequel l'oléfine est le propylène.

 9. Procédé selon la revendication 1, dans lequel M est choisi parmi le groupe constitué par le zirconium et le hafnium.

55 10. Procédé selon la revendication 1, dans lequel le métallocène neutre est choisi parmi le groupe constitué par le diméthyl éthylènebis(tétrahydroindényle)zirconium, le diméthyl éthylènebis(indényle) zirconium, le diméthyl éthylènebis(indényle) hafnium et le diméthyl isopropylidène(cyclopentadiényle-1-fluorényl) zirconium.

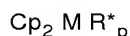
 11. Procédé selon la revendication 1, dans lequel le composé ionique ionisant est le tétrakis(pentafluorophényl) borate

de triphénylcarbénium.

12. Procédé selon la revendication 1, dans lequel on prépare le catalyseur en passant par les étapes ci-après consistant à :

- a) mélanger un composé ionique ionisant avec un métallocène neutre ; et
b) mettre en contact le composé ionique ionisant et le métallocène neutre pour générer une paire d'ions dans laquelle le cation de métallocène fait office de catalyseur

dans lequel le métallocène neutre répond à la formule générale



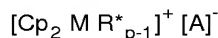
où Cp représente un groupe cyclopentadiényle ou un groupe cyclopentadiényle substitué, chaque groupe Cp étant identique ou différent, R* représente un radical hydrocarbyle, les radicaux R* étant identiques ou différents, M représente le titane, le zirconium ou le hafnium, p est égal à 1 - 4 ;
dans lequel le composé ionique ionisant ne contient pas un proton actif et contient un cation de carbonium, d'oxonium ou de sulfonium, et
dans lequel l'anion du composé ionique ionisant n'est pas coordonné ou est coordonné seulement de manière lâche au cation de métallocène et est chimiquement inerte vis-à-vis du cation de métallocène.

13. Système de catalyseur comprenant :

- a) un catalyseur à base de métallocène ; et
b) un alkylaluminium

dans lequel l'alkylaluminium répond à la formule générale AlR'_3 où R' représente un groupe alkyle contenant jusqu'à 6 atomes de carbone ;

dans lequel le catalyseur du type d'un métallocène représente une paire d'ions répondant à la formule générale



où $[\text{Cp}_2 \text{ M R}^*_{p-1}]^+$ représente un cation de métallocène dans lequel Cp représente un groupe cyclopentadiényle ou un groupe cyclopentadiényle substitué, chaque groupe Cp étant identique ou différent, R* représente un radical hydrocarbyle, les radicaux R* étant identiques ou différents, M représente le titane, le zirconium ou le hafnium, p est égal à 1 - 4 ;

dans lequel le métallocène représente une paire d'ions formée à partir d'un composé de métallocène neutre et d'un composé ionique ionisant, ladite paire d'ions comprenant un cation de métallocène et un anion provenant du composé ionique ionisant ;

dans lequel le composé ionique ionisant ne contient pas un proton actif et répond à la formule générale $[\text{C}][\text{A}]$ où [C] contient un cation carbonium, un cation oxonium ou un cation sulfonium et l'anion [A] n'est pas coordonné ou est coordonné seulement de manière lâche au cation de métallocène ;

à l'exclusion du système de catalyseur dans lequel

- (i) l'alkylaluminium est le triméthylaluminium ;
(ii) le composé de métallocène neutre est le diméthyl isopropylidène (cyclopentadiényl-1-fluorényl) zirconium ;
et
(iv) le composé ionique ionisant est le tétrakis (pentafluorophényl) borate de triphénylcarbénium.

14. Système de catalyseur selon la revendication 13, dans lequel R* représente un groupe alkyle, un groupe aryle, un groupe alcényle, un groupe alkylaryle ou un groupe arylalkyle contenant jusqu'à 20 atomes de carbone.

15. Système de catalyseur selon la revendication 13, dans lequel R* représente un groupe alkyle contenant jusqu'à 6 atomes de carbone ou un groupe aryle contenant jusqu'à 10 atomes de carbone

16. Système de catalyseur selon la revendication 13, dans lequel l'alkylaluminium est choisi parmi le groupe constitué

par le triéthylaluminium et le triméthylaluminium.

17. Système de catalyseur selon la revendication 16, dans lequel l'alkylaluminium est le triéthylaluminium.

5 18. Système de catalyseur selon la revendication 13, dans lequel le métallocène neutre est choisi parmi le groupe constitué par le diméthyl éthylènebis(tétrahydro-indényl)zirconium, le diméthyl éthylènebis(indényl) zirconium, le diméthyl éthylènebis(indényl) hafnium et le diméthyl isopropylidène(cyclopentadiényl-1-fluorényl) zirconium.

10 19. Système de catalyseur selon la revendication 13, dans lequel l'anion est l'anion tétrakis(pentafluorophényle) borate.

15

20

25

30

35

40

45

50

55